SOUTHERN CALIFORNIA PARTICLE SUPERSITE

Progress Report for Period July 1, 2003 – September 30, 2003

United States Environmental Protection Agency

Principal Investigator: John R. Froines, Ph.D., UCLA School of Public Health

Co-Principal Investigator: Constantinos Sioutas, Sc.D., USC School of Engineering

1. Introduction

The overall objective of the Southern California Particle Supersite is to conduct research and monitoring that contributes to a better understanding of the measurement, sources, size distribution, chemical composition and physical state, spatial and temporal variability, and health effects of suspended particulate matter (PM) in the Los Angeles Basin (LAB). This report addresses the period from July 1, 2003 to September 30, 2003. It is divided into 9 sections, each addressing a specific research area. Furthermore, a major portion of the information included in this report has been either submitted or accepted for publication in peer-reviewed journals. Below is a list of manuscripts either submitted or accepted for publication which were produced through the Southern California Supersite funds and in which the EPA Supersite program has been acknowledged.

2. Publications

The Southern California Particle Supersite has been acknowledged so far in the following publications:

1. Misra, C., Geller, M., Sioutas, C and Solomon P. "Development and evaluation of a continuous coarse particle monitor". *Journal of Air and Waste Management Association*, 51:1309-1317, 2001

2. Geller, M.D., Kim, S. Misra, C., Sioutas, C., Olson, B.A and Marple, V.A. "Methodology for measuring size-dependent chemical composition of ultrafine particles " *Aerosol Science and Technology*, 36(6): 748-763, 2002

3. Misra, C., Kim S., Shen S. and Sioutas C. "Design and evaluation of a high-flow rate, very low pressure drop impactor for separation and collection of fine from ultrafine particles". *Journal of Aerosol Science*, 33(5): 735-752, 2002

4. Li, N., Kim, S., Wang, M., Froines, J.R., Sioutas, C. and Nel, A. "Use of a Stratified Oxidative Stress Model to Study the Biological Effects of Ambient Concentrated and Diesel Exhaust Particulate Matter". *Inhalation Toxicology*, 14(5): 459-486, 2002

5. Zhu, Y., Hinds, W.C., Kim, S and Sioutas, C. "Concentration and Size Distribution of Ultrafine Particles near a Major Highway". *Journal of Air and Waste Management Association*, 52:1032-1042, 2002

6. Singh, M., Jaques, P. and Sioutas, C. "Particle-bound metals in source and receptor sites of the Los Angeles Basin". *Atmospheric Environment,* 36(10): 1675-168, 2002

7. Kim, S., Shi, S., Zhu, Y., Hinds, W.C., and Sioutas, C. "Size Distribution, Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the Los Angeles Basin". *Journal of Air and Waste Management Association*, 52:174-185, 2002

8. Misra, C., Singh, M., Hall, P. and Sioutas, C. "Development and evaluation of a personal cascade impactor sampler (PCIS)". *Journal of Aerosol Science,* 33(7), 1027-1047, 2002

9. Eiguren-Fernandez A., Miguel A.H, Jaques, P. and Sioutas, C. "Evaluation of a Denuder-MOUDI-PUF Sampling System to Determine the Size Distribution of Semivolatile Polycyclic Aromatic Hydrocarbons in the Atmosphere". *Aerosol Science and* Technology, 37: 201-209, 2003

10. Fine, P.M., Hering, S.V., Jaques P.A. and Sioutas, C. "Performance Evaluation and Field Use of a Continuous Monitor for Measuring Size-Segregated PM2.5 Particulate Nitrate". *Aerosol Science and Technology*, 37: 342-354, 2003

11. Singh, M., Misra, C., and Sioutas, C. "Field Evaluation of a Particle Monitor for Size-Dependent Measurement of Mass and Chemical Composition of Individual Exposures to PM". *Atmospheric Environment,,* in press, June 2003.

12. Shen, S., Zhu, Y., Jaques PA and Sioutas C. "Evaluation of the SMPS-APS system as a Continuous Monitor for PM2.5 and PM10". *Atmospheric Environment*, 36, 3939-3950, 2002

13. Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C. "Study on Ultrafine Particles and other Vehicular Pollutants near a Busy Highway". *Atmospheric Environment*. 36, 4375-4383, 2002

14. Misra, C., Geller, M.D., Solomon, P.A. and Sioutas, C. "Development of a PM10 Inertial Impactor for Coarse Particle Measurement and Speciation." *Aerosol Science and Technology,* 37:271-282, 2003

15. Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C. "Seasonal Trends of Concentration and Size Distributions of Ultrafine Particles Near Major Freeways in Los Angeles". *Aerosol Science and Technology,* in press, April 2003

16. Misra, C., Geller, M., Fine, P.M.. and Sioutas, C. "Development and Evaluation of an Ultrafine Particle Concentrator Facility for Human Exposures". *Aerosol Science and Technology*, 38, 27-35, 2004.

17. Gong, H.Jr, Linn, W.S., Sioutas, C., Terrell S.L., Clark, K.W., Anderson K.R and Terrell, L . "Controlled Exposures of Healthy and Asthmatic Volunteers to Concentrated Ambient Fine Particles in Los Angeles". *Inhalation Toxicology*, 15(4), 305-325, 2003

18. Li, N., Sioutas, C , Froines, J.R., Cho, A., Misra, C and Nel, A., "Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage" *Environmental Health Perspectives*, in press, December 2002

19. Chakrabarti, B., Singh, M and Sioutas C. "Development of a Continuous Monitor For Measuring the Mass Concentration of Ultrafine PM." *Aerosol Science and Technology*, in press, January 2003

20. Jaques, P.A., Ambs, J.L. and Sioutas, C. "Field Evaluation Of The Differential TEOM® Monitor For Continuous PM2.5 Mass Concentrations ". Submitted to *Aerosol Science and Technology*, September 2002

21. Zhu, Y., Hinds, W.C. and Sioutas, C. "Vertical Profile of Ultrafine Particles in the Vicinity of a Major Highway". Submitted to *Atmospheric Environment*, December 2002

22. Fine, P.M., Si, S., Geller, M.G., and Sioutas, C. "Diurnal and Seasonal Characteristics and Size of Ultrafine PM in Receptor Areas of the Los Angeles Basin". *Aerosol Science and Technology*, in press, 2003

23. Chakrabarti, B., Fine, P.M, Delfino R.J. and Sioutas C. "Performance Evaluation of an active personal DataRAM PM2.5 mass monitor (Thermo Anderson pDR-1200) designed for continuous personal exposure measurements" *Atmospheric Environment*, in press, August 2003.

24. Yu, R.C., Teh, H.W., Sioutas, C. and Froines, J.R. "Quality Control of Semi-Continuous Mobility Size-Fractionated Particle Number Concentration Data". *Atmospheric Environment*, in press, July 2003

25. Miguel, A.H., Eiguren-Fernandez, A., Jaques, P.A., Mayo, P.R. and Sioutas, C. "Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California" *Atmospheric Environment*, in press, July 2003

26. Sardar, S.B., Fine, P.M., Jaques, P.A., Sioutas, C. "Seasonal and Spatial Variability of the Size-Resolved Chemical Composition of $PM_{2.5}$ in the Los Angeles Basin." Submitted to *Atmospheric Environment*, June 2003

27. Geller, M.D., Fine, P.M., Sioutas, C. "The Relationship between Both Real-time and Time-integrated Coarse (2.5 – 10 μm), Intermediate (1 – 2.5 μm), and Fine (0 – 2.5 μm) Particulate Matter in the Los Angeles Basin." Submitted to *Journal of the Air and Waste Management Association*, June 2003.

28. Eiguren-Fernandez, A., Miguel, A.H., Froines, J.R., Thurairatnam, S., Avol, E. "Seasonal and Spatial Variation of Polycyclic Aromatic Hydrocarbons in Vapor-Phase and $PM_{2.5}$ in Southern California Urban and Rural Communities" Submitted to *Atmospheric Environment*, June 2003.

29. Reisen, F., Wheeler, S. and Arey, J. "Methyl- and Dimethyl-/Ethyl-Nitronaphthalenes Measured in Ambient Air in Southern California" accepted by *Atmospheric Environment,* June 2003.

30. Cho A.K., Sioutas C., Schmitz, D.A., Kumagai Y., Misra C., Singh M., Miguel A.H and Froines, J.R. "Redox activity of airborne particulate matter (PM) at different sites in the Los Angeles Basin" Submitted to *Atmospheric Environment*, June 2003

31. Jaques, P.A., Ambs, J.L., Hering, S.V., Fine, P.M. and Sioutas, C. " Field Assessment of the Dynamics of Particulate Nitrate Vaporization Using Differential TEOM® and Automated Nitrate Monitors ". Submitted to *Atmospheric Environment*, July 2003

32. Fine, P.M., Chakrabarti, B, Krudysz M., Schauer J.J. and Sioutas, C. "Seasonal, Spatial, and Diurnal Variations of Individual Organic Compound Constituents of Ultrafine and Accumulation Mode PM in the Los Angeles Basin".   Submitted to *Environmental Science and Technology*, July 2003.

3. PIU Sampling Location and Status

A key feature of our Supersite activities has been in the ability to conduct state-of the art measurements of the physiochemical characteristics of PM in different locations of the Los Angeles basin (LAB). We originally proposed a 2.5-year repeating cycle of measurements at five locations. Each location has been scheduled to sample during a period of intense photochemistry (defined approximately as May-October) and low photochemical activity (defined as the period between November-April). During the period of this progress report, we've continued PM sampling with the Particle Instrumentation Unit (PIU) at the University of Southern California (USC), the fifth Southern California Supersite location, beginning September 2002. The site is located about one mile directly south of downtown Los Angeles and the 10 Freeway, which runs east to west, and is about 100 meters directly east of the 110 Freeway. The site is embellished with typical urban sources: centralized within a major congested urban

center; adjacent to several 2 – 7 story buildings; adjacent to pedestrian and local traffic as well as central arteries; and near building and road construction projects. Since the site is about 15 miles directly east north east of the ocean, prevailing winds are primarily from the west and southwest during most of the daytime when mobile and stationary emission sources may be expected to predominate. However, the nearby relatively large buildings can also disturb the winds, affecting urban canyon and wake properties. These factors consist of turbulent winds and updrafts that may confound local measurements of regional wind trajectories, and increase the delivery of local sources (e.g., construction debris, and larger settled particles from road related vehicle wear-and-tear) in addition to the close-by 110 Freeway. Several studies are being conducted as we enter the third quarter at the USC site to investigate local source contributions in addition to the regional transported emissions that may generally come from the west freeways.

We have completed all Metal/Element speciation, Ion, and EC/OC analysis for integrated samples, through to the end of June. In early June, we finalized size integrated on-line measurements of particulate nitrate and carbon using the Integrated Collection and Vaporization System (ICVS) developed by Aerosol Dynamics Inc. Additionally, paired semi-continuous PM2.5 measurements using a prototype Differential TEOM, designed to measure "non-artifact" laden mass, has been completed. Two continuous BAM monitors continue to operate: one, with the standard PM2.5 inlet, the second with an ultrafine inlet (designed at the USC lab). Coupled with our USC-TEOM coarse monitor, time-integrated mass measurements are being compared to those by our SMPS-APS, MOUDI, Partisol, and other filter mass samplers for longer sample integrals, overall, resulting in paired integrated semi-continuous, diurnal, and 24-hour mass measurements of coarse, fine, and ultrafine PM.

We have continued to make our mobile particle trailer available for co-located exposure studies. The following health studies have been supported by the Supersite measurements: In vitro studies undertaken by Drs. Andre Nel and Arthur Cho (UCLA) investigating the hypotheses that organic constituents associated with PM, including quinines, other organic compounds (PAHs, nitro-PAHs, and aldehydes/ketones) and metals are capable of generating reactive oxygen species (RQS) and acting as electrophilic agents. These are ongoing studies. Animal inhalation toxicology studies using Concentrated Ambient Particulates (CAP) investigating the hypotheses that atmospheric chemistry is important in the toxicity of PM and co-pollutants, airway injury and cardiovascular effects will be greater at receptor sites downwind of source sites along the mobile source trajectory in the Los Angeles basin. Led by Drs. Harkema (University of Michigan), Kleinman (UC Irvine), Froines, and Nel (UCLA), these co-located studies have commenced during our first month at the USC site and have continued periodically to the present. A demonstrative-level cooperative project of the California Air Resources Board and the Supersite was initiated during the winter of 2003 to evaluate the nature of PM and gaseous pollutants in various microenvironments of Southern California, especially those impacted by vehicular traffic. Gaseous pollutants evaluated included carbon monoxide, carbon dioxide, and oxides of nitrogen using advanced monitoring equipment including ultrafine PM counters and sizers as well as carbon, PM 2.5, and PAH monitors placed in an electrically powered Toyota RAV4. Data reporting resolution was one minute or less with operations of the study closely linked to the

Supersite, its instrumentation and staff.

4. Time integrated, size fractionated mass and chemical speciation for five sites in the Los Angeles Basin.

Sampling and chemical analysis of PM for the month of May and June 2003 were done at USC PIU. The results for this report are given in the Figures 1 through 6. In Figure1 at USC the coarse mode dominated the PM followed by the accumulation mode. The PM levels increased in summer as compared to the winter months. In Fig 2 at USC nitrate and metals dominates the coarse mode for the months of May and June 2003. During these months nitrate contribution to the coarse mode increased as compared to the winter months resulting from photochemical formation of nitrate particles. In the month of June, a summer month, sulfate is also observed to be high and have resulted from particle formation by photochemistry at this site. In Figure 3, nitrate and organics dominated the accumulation mode. In this mode during summer the sulfate level has shown an increase as compared to the earlier winter months, which have resulted from photochemical formation of sulfate particles. The ultrafine mode (Fig 4) is dominated by OC as for the rest of the months and sites. Interestingly contributions of sulfate and metals are found during the month of May and June at USC in the ultrafine mode. The increase of sulfate is due to the photochemistry involved while the metals in this site may have been the contributions of lube oils from traffic at USC, which is a source site. In Figure 5 at USC and in the months of May and June OC concentration is more in ultrafine and accumulation mode in line with results previously narrated. Both the months of May and June at USC showed the predominance of EC (Fig 6) in the ultrafine mode as expected because USC is a source site and the EC is emitted in primary emissions from diesel vehicles in this mode. A high coefficient of statistical determination, R^2 of 0.65, was found for USC between EC and OC. USC is a source site and this high R^2 is indicative of primary emissions from vehicular source.

Currently sampling is going on at USC PIU and new results will be added during the presentation of next report.

Table 1

Site	Period of Sampling
Downey	**Oct 2000 – Feb 2001**
Riverside	**Feb 2001 – June 2001**
Rubidoux	**June 2001 – Sept 2001**
Claremont	**Sept 2001 – Aug 2002**
USC	**Oct 2001 – Ongoing**

Table 2 . Averaged OC/EC ratios and correlation coefficients at source and receptor sites

Source site	Average and Std Dev	Range	R^2
Downey	5.08 ± 2.3	$2.7 - 9.57$	0.81
USC	5.80 ± 1.83	$2.85 - 9.68$	0.65

Receptor site	Average and Std Dev	Range	R^2
Rubidoux	7.78 ± 1.76	$6.6 - 8.9$	0.57
Riverside	6.05 ± 3.55	$3.6 - 15.2$	0.64
Claremont	14.84 ± 8.2	$4.4 - 35.7$	0.38

The correlation coefficients between measured metal concentrations in the coarse and fine (accumulation plus ultrafine) modes at receptor and source sites are given in Table 3. Only the more significant correlations are included ($r^2 > 0.6$). In the coarse mode at the source sites, high correlations are observed for many of the elements. The highest correlations suggest a common source of Al and Si, and a related source of Fe, Ti, Mn, Zn, and Cu. The major source of coarse particles is soil and road dust, and these elements can all be of crustal origin. In the fine mode and at the source sites, the degree of correlation among elements drops significantly. Fine particles have more varied sources than coarse particles, and thus inter-element correlations are reduced by varying contributions of multiple sources of the same element. The results show moderately high correlations among some metals (Fe, Si, Mn, Zn), which may originate from crustal, vehicular, or industrial sources. Additional high correlation coefficients were observed in the coarse mode at the receptor sites between Al and Si and some other crustal metals indicating a soil/road dust source. Unlike the coarse mode, no significant correlations were observed in the fine mode at the receptor sites. In general, less correlation is expected at the downwind receptor sites due to the potential influence of a greater variety of sources upwind.

Table 3 Significant ($R^2 > 0.6$) Correlation between 24-h averaged mass concentrations of selected metals at source and receptor sites

Source Sites (Downey/USC)

	Coarse mode			Fine mode	
Metal vs.	**Metal**	**R^2**	**Metal vs.**	**Metal**	**R^2**
Al	Si	0.98	Si	Fe	0.81
Al	Fe	0.83	Si	Mn	0.69
Al	Ti	0.72	Si	Zn	0.72
Al	Mn	0.81	Fe	Ti	0.81
Al	Zn	0.66	Fe	Mn	0.67
Si	Fe	0.81	Fe	Cu	0.67
Si	Ti	0.71	Fe	Zn	0.72
Si	Mn	0.79	Mn	Zn	0.81
Si	Zn	0.66			
Fe	Ti	0.96			
Fe	V	0.79			
Fe	Mn	0.96			
Fe	Cu	0.90			
Fe	Zn	0.92			
Ti	V	0.86			
Ti	Mn	0.96			
Ti	Cu	0.94			
Ti	Zn	0.92			
V	Mn	0.85			
V	Cu	0.88			
V	Zn	0.81			

Receptor Site (Claremont/Riverside/Rubidoux)
Coarse mode

Metal vs.	**Metal**	**R^2**
Al	Si	0.92
Al	Fe	0.64
Al	Mn	0.81
Al	Cu	0.66
Mn	Cu	0.71

Figure 1.
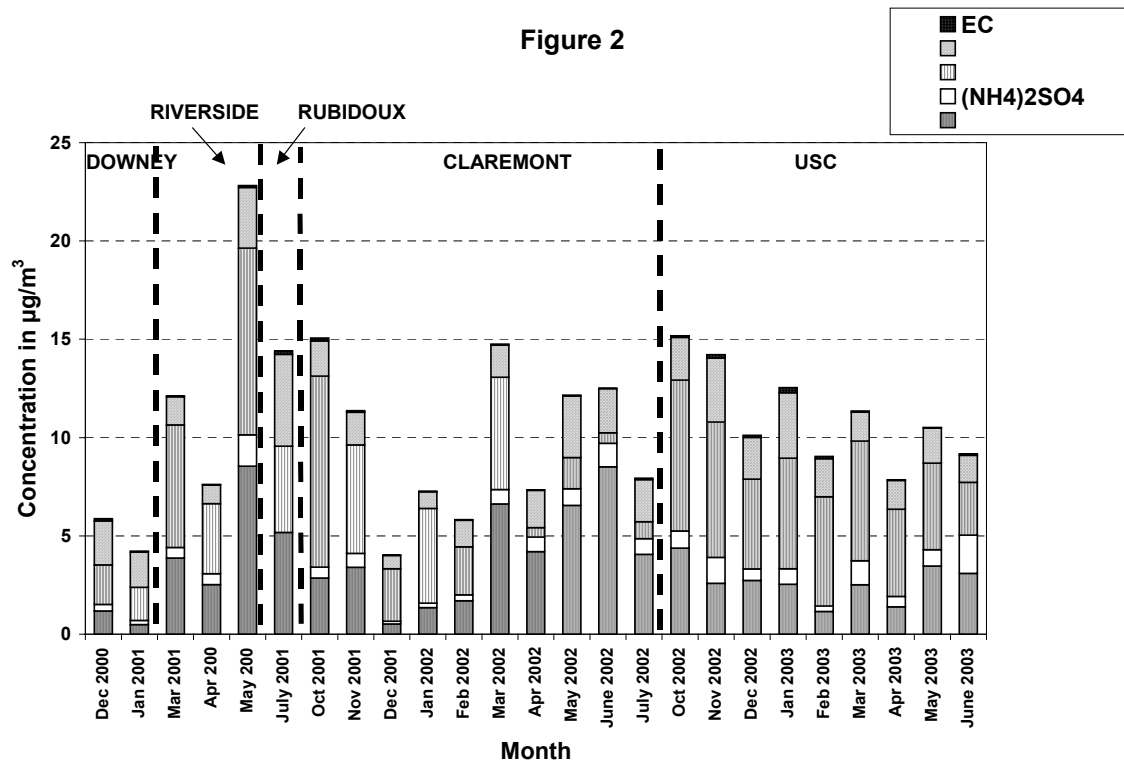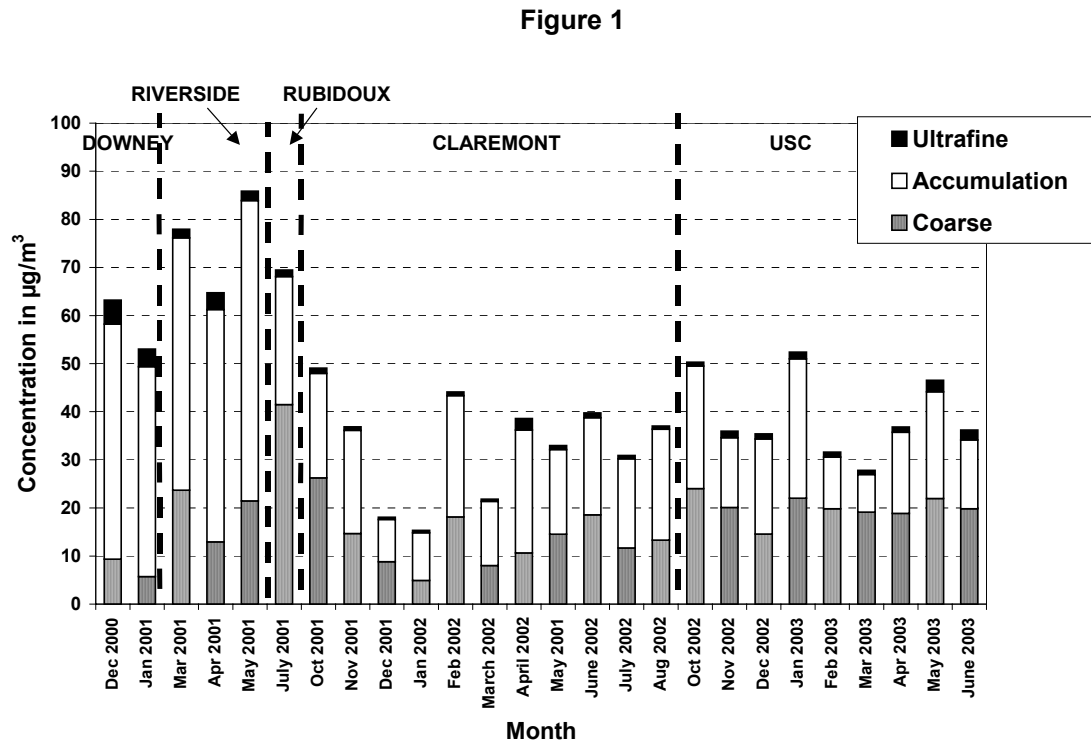
Figure 1
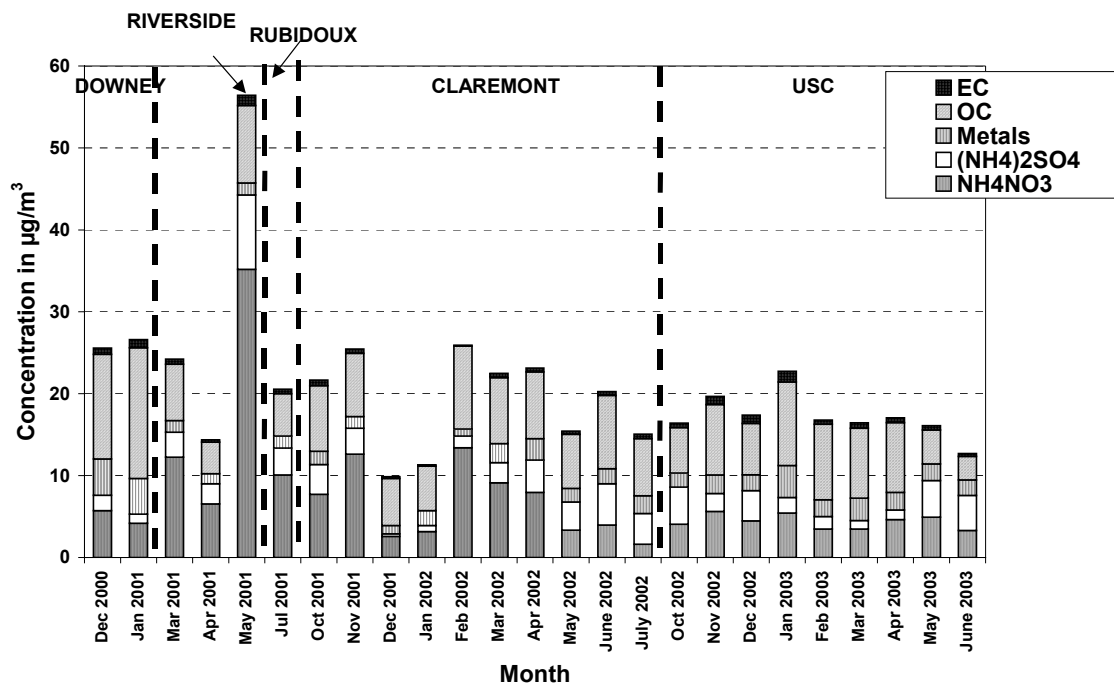
Figure 2
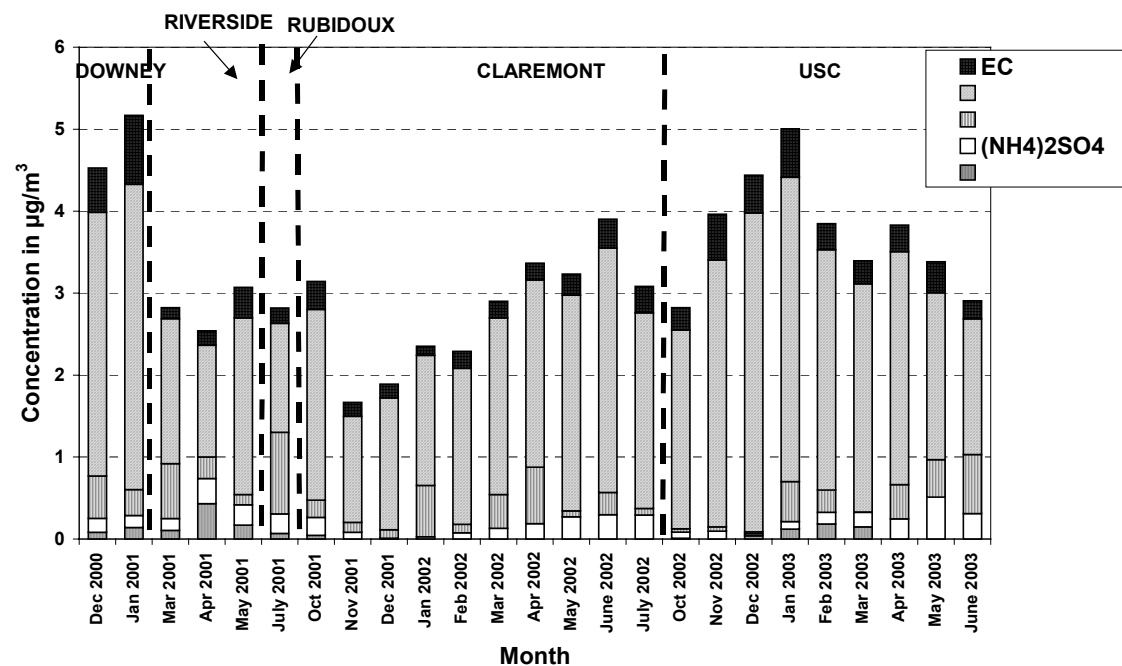
Figure 3

Figure 4

Figure 5
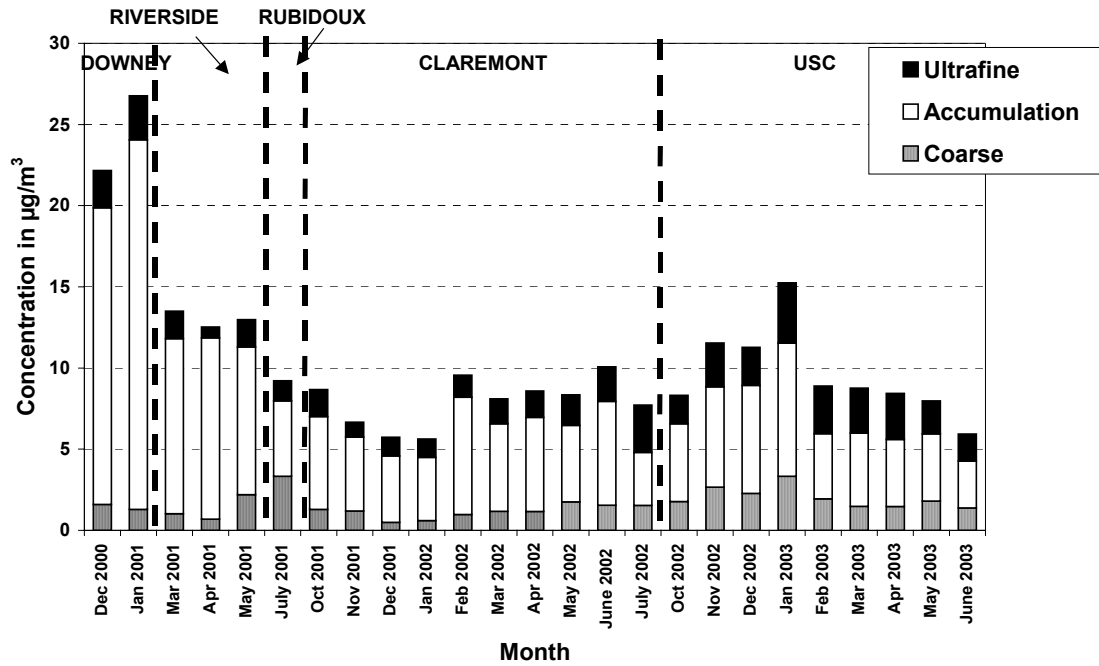
Figure 6
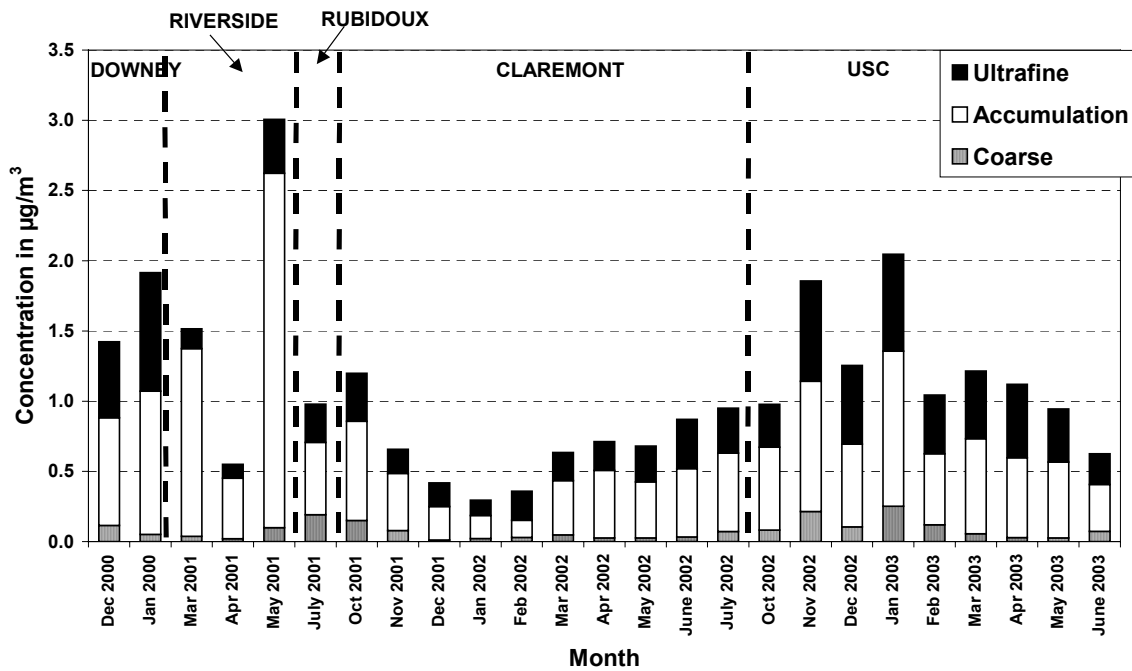
5. Characterization of PAH and PAH-Derivatives

Janet Arey and Fabienne Reisen
Air Pollution Research Center
University of California, Riverside

Results of Ambient Measurements

A manuscript entitled "Atmospheric Reactions Influence Seasonal PAH & Nitro-PAH Measurements in the Los Angeles Basin" by Fabienne Reisen and Janet Arey and describing our results from sampling in the summer at Los Angeles (August 12-16, 2002) and Riverside (August 26-30, 2002) and in the winter at Los Angeles (January 13-17, 2003) and Riverside (January 27-31, 2003) is nearly ready for submission.

The sampling consisted of three daytime samples of 3.5 hrs each and one nighttime sample of 11.5 hrs. The sampling times (given in local time) were chosen to emphasize direct emissions (early morning, 7-10:30, labeled "Morning" on Figures), the period at highest expected photochemical activity (11-14:30, labeled "Day" on Figures), the period around sunset when NO_3 chemistry could begin (15-18:30, labeled "Evening" on Figures) and an overnight sample (19-6:30, labeled "Night" on Figures). As illustrated by the figures below, ambient PAH concentrations were highest in Los Angeles during January, as a result of traffic input at the source site and tighter inversions during winter. In contrast, nitro-PAH levels were highest in Riverside during August, as a result of more photochemistry during summer. Thus, the [nitro-PAH]/[PAH] yields were significantly higher in the summer than winter and at the receptor site in Riverside.
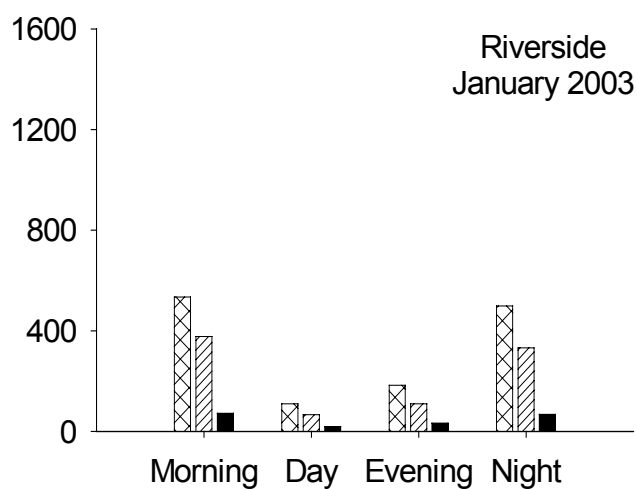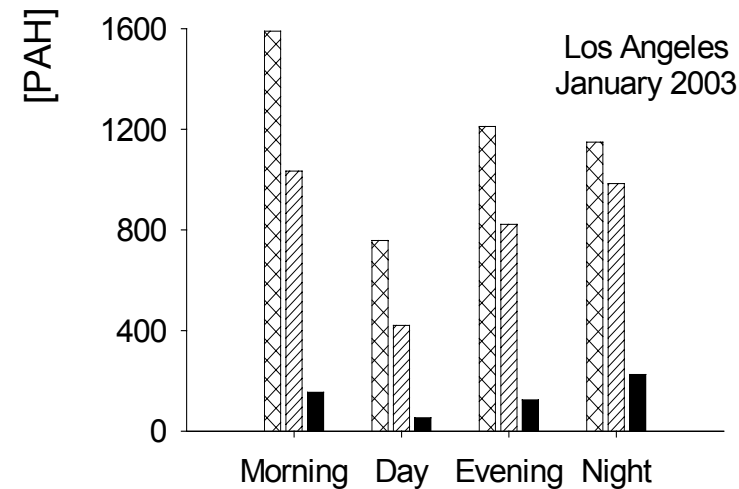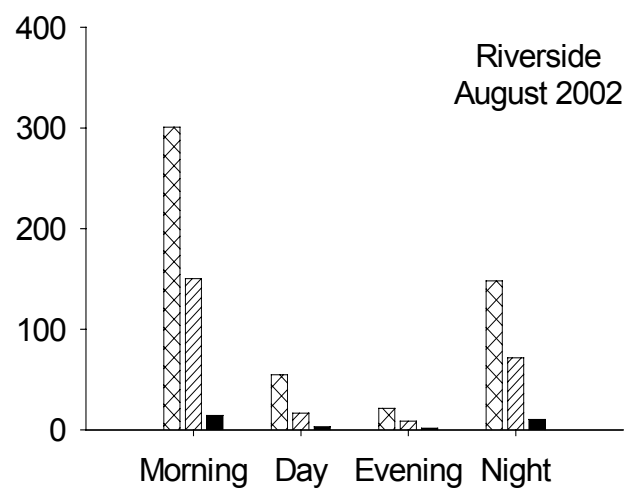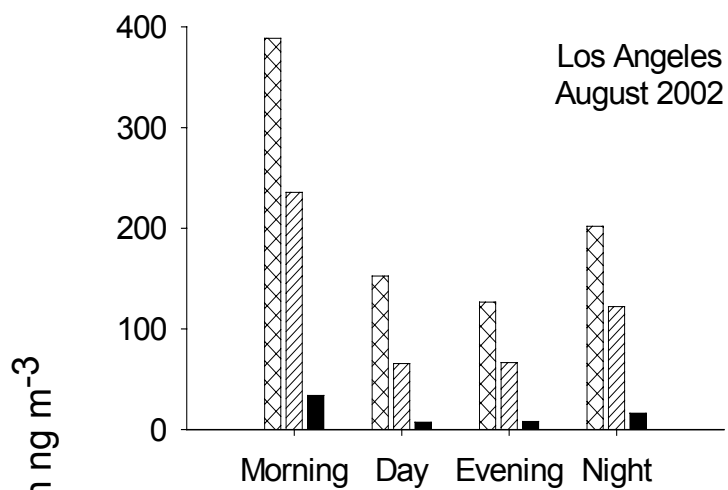
Diurnal, seasonal and spatial variations of ambient concentrations of naphthalene (cross hatched), 1 + 2-methylnaphthalenes (diagonal hatched) and dimethylnaphthalenes + ethylnaphthalenes (black bars).
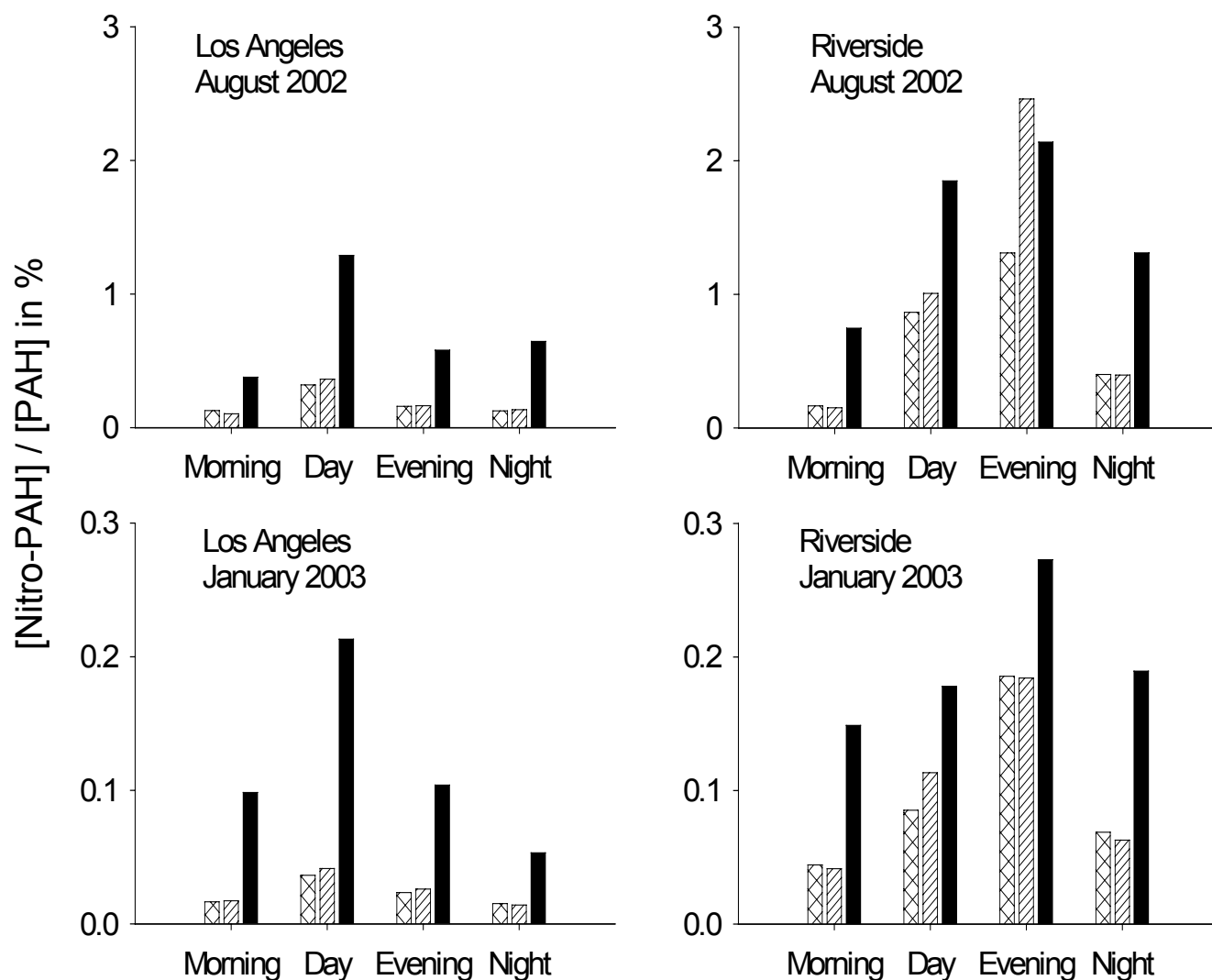
Diurnal, seasonal and spatial variations of the ratios of [Nitro-PAH]/[PAH] (in %) for [nitronaphthalenes]/[naphthalene] (cross-hatched), [methylnitronaphthalenes]/[methylnaphthalenes] (diagonally hatched) and [dimethylnitronaphthalenes & ethylnitronaphthalenes]/[dimethylnaphthalenes & ethylnaphthalenes] (black bars).

Preliminary Chamber Reactions

Phthalic acid and 4-methyl-phthalic acid have been suggested as markers of secondary particle formation. Preliminary results of chamber reactions of naphthalene and 2-methylnaphthalene suggest that low yields of phthalic acid and 4-methyl-phthalic acid can be produced in these gas-phase hydroxyl (OH) radical-initiated reactions, in which a large fraction of the starting PAH is consumed and secondary reactions of initial product species may be

expected to occur. This work is on going and additional methods development is required before yields for these acid products can be reliably determined.

6. Predicting Ultrafine Particles near Major Freeways

Recent toxicology studies have demonstrated that atmospheric ultrafine particles are responsible for some of the adverse health effects. Motor vehicle emissions usually constitute the most significant source of ultrafine particles (diameter < 100 nm) in an urban environment, yet, little is known about the concentration and size distribution of ultrafine particles in the vicinity of major highways.

The present research focuses on developing a model to determine ultrafine particle behavior after emissions, as they are transported away from the emission source --- a freeway. Although discrepancies exist between the predicted and measured particle size distributions, the model predicts the total particle number concentration very accurately by use of an atmospheric dispersion model alone. This implies that atmospheric dispersion is by far the most important mechanisms in determining particle number concentration near freeways. Other aerosol or chemical processes may have an effect on the particle size distribution but not on total particle number concentrations. Thus, the model developed in this study provides epidemiologists and others concerned with the health effects of motor vehicles with a simple tool to estimate ultrafine particle number concentrations near freeways for health related studies.

The model uses traffic information, which includes traffic volume, traffic composition, and particle number emission factors for each vehicle categories, and meteorological data, such as wind direction and speed, turbulence parameter, γ, which is related to atmospheric stability class, as model input and predicts ultrafine particle number concentrations at certain downwind distance from the freeway.

Figures 1a-b were prepared to compare the model predicted particle number concentrations near the 405 and 710 freeways with experimental data. The turbulence parameters used in Figures 1a-b were the best-fitted γ values based on our CO data. In the literature, limited particle number concentration emission factors have been reported. And, these limited data cover a wide range mainly due to two factors. The first one is different driving pattern that includes different driving speeds, fuel usage, traffic compositions, etc. Among these factors the vehicle speed seems to be the most important one. Much higher particle number concentrations have been reported from fast driving vehicles especially when vehicles are faster than 120 km/hr. The second one is the use of different particle detecting instruments that measure particles in different size ranges by different research groups. Since a large fraction of freshly emitted particles are in the smallest ultrafine size range (<10 nm), an instrument that has a larger lower-cutoff size will report a smaller number concentration. To illustrate how sensitive the model would be to emission factors, the highest, lowest and the best-fit particle number emission factors were used in Figures 1a-b. Their values are summarized in Table 1. The total fleet was decomposed into two categories, heavy-duty diesel vehicles and gasoline-powered vehicles. Line source strength for particle number concentration was defined by the following equation:

$$Q_{line} = E_{gasoline} \times V_{gasoline} + E_{diesel} \times V_{diesel} \qquad (1)$$

where $E_{gasoline}$ and E_{diesel} are particle number emission factors from gasoline-powered vehicles and heavy-duty diesel trucks (particle/vehicle/m), respectively; $V_{gasoline}$ and V_{diesel} are traffic volume of gasoline-powered vehicles and heavy-duty diesel trucks in the fleet (vehicle/sec). It is seen in Figure 1, model predicted particle number concentration is directly proportional to the line source strength, Q_{line}. Since E_{diesel} is usually much greater than $E_{gasoline}$, Q_{line} is more sensitive to V_{diesel}.

The best-fit emission factors used in the model were based on our summer freeway study data.(Zhu et al. 2002a; Zhu et al. 2002b) The average ambient temperature during our experiment is about 30 Celsius.(Zhu et al. 2003) Particle emission factors are highly dependent on ambient temperature(Kittelson 1998). Zhu et al., (2003) reported dramatically different ultrafine particle size distributions in winter season. Thus, to apply the current model to other ambient temperature conditions, proper emission factors should be selected from the literature. It should be also noted, particle emission factors also highly dependent on traffic speed. The best-fit emission factors in the current model are based on highway-speed data. To apply the model to busy streets, lower emission factors have to be assumed.

Another influence factor in the model is the turbulent parameter, γ. In the current model, γ=0.16, is determined from our CO data. Our measurements were all done in sunny days from around 10 am to 4 pm, when atmospheric stability class was A (Zhu et al. 2002a; Zhu et al. 2002b). Under other meteorological conditions, γ may be other values.
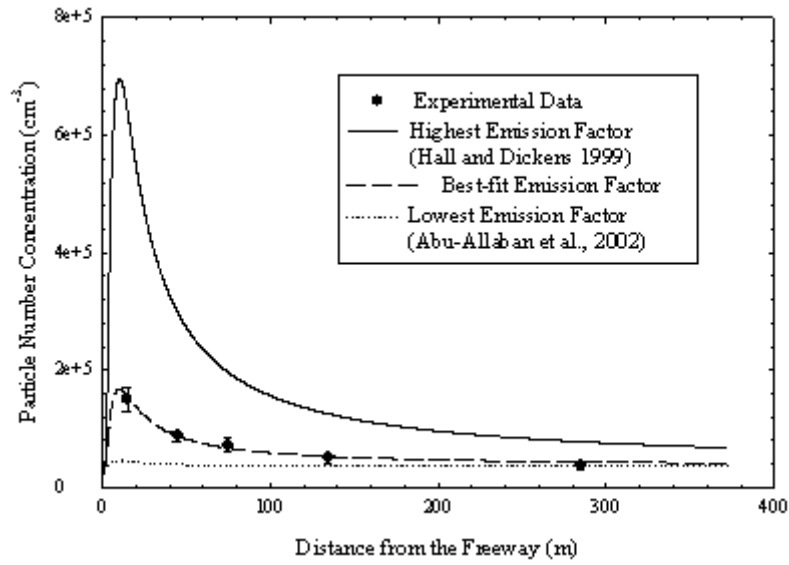
Table 1. Particle Number Concentration Emission Factors

Emission Factor (particle/vehicle/m)	Heavy-duty Diesel Trucks	Gasoline-powered Vehicles	Reference
Highest	5.0e12	2.0e12	Hall and Dickens 1999
Best-fit	1.0e12	4.0e11	N/A
Lowest	2.8e11	1.8e10	Abu-Allaban et al., 2002

**REFERENCES:**

Kittelson, D. B. (1998). Engines and Nanoparticles: A Review, *Journal of Aerosol Science*. 29:575-588.

Zhu, Y., Hinds, W. C., Kim, S. and Sioutas, C. (2002a). Concentration and Size Distribution of Ultrafine Particles near a Major Highway, *Journal of Air and Waste Management Assoc.* 52:174-185.

Zhu, Y., Hinds, W. C., Kim, S., Shen, S. and Sioutas, C. (2002b). Study of Ultrafine Particles near a Major Highway with Heavy-duty Diesel Traffic, *Atmospheric Environment*. 36:4323-4335.

Zhu, Y., Hinds, W. C., Shen, S. and Sioutas, C. (2003). Seasonal trends of concentration and size distribution of ultrafine particles near major highways in Los Angeles, *Accepted for publication in Aerosol Science and Technology*.

(a)
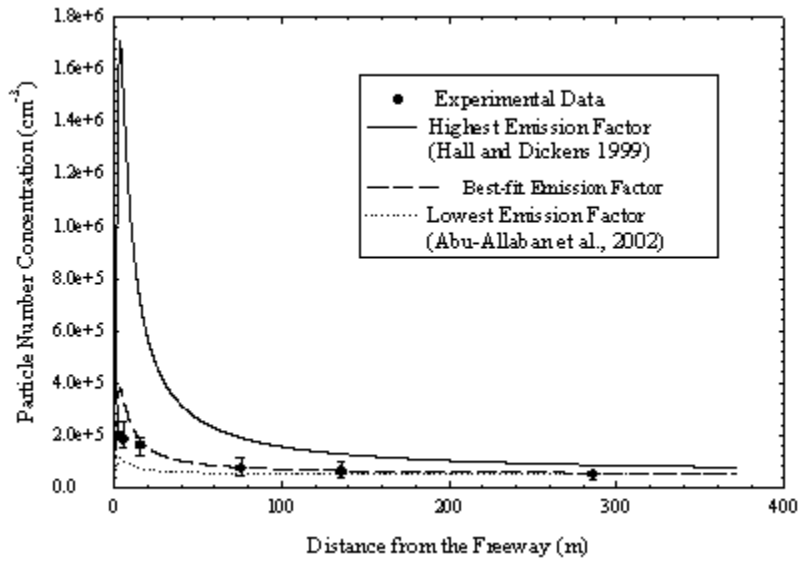
(b)

Figure1. Model predicted total particle number concentration near (a) the 405 freeway and (b) the 710 freeway in summer.

7. Chemical Characterization of Ultrafine Particles in the LA Basin

The plan for this study is to conduct bi-weekly MOUDI/Nano-MOUDI sampling in the following sites*:

Table 1. *Shaded dates indicate completed and/or in progress.

Date	USC	Long Beach	Riverside	Upland
Fall	Oct. 2-Oct. 16	Oct. 16-Oct. 30	Oct. 30-Nov.13	Nov. 13-Nov. 27
Winter	Feb. 27-Mar. 13	Mar. 13-Mar. 27	Jan. 27-Feb. 13	Feb. 13-Feb. 27
Spring		May. 20-June. 2		
Summer	July 15-July 28	July 29-Aug.11	Aug.12-Aug.25	Aug.26-Sept.8

Progress To-Date:

Fourteen-day composite size-fractionated PM2.5 and UF impactor samples were collected and analyzed. The sampling is conducted over four seasons (autumn, winter, spring/marine layer, summer) and at four sites, including upwind source and downwind, inland receptor sites in the LAB as shown in the above table. Aluminum substrates were pre-baked and sealed prior to June 30, 2003. Six substrates per two-week period were used. The MOUDI/Nano-MOUDI combination was employed at each site listed above from June 30, 2003 to August 25, 2003. The summer sampling has been done during the period of this report. Sampling was continuous for the listed periods with no change of substrates except between sites. Samples were collected on aluminum substrates and analyzed for gravimetric mass, sulfate and nitrate by ion chromatography, and elemental and organic carbon by thermal evolution/optical transmission analysis. Data on size-segregated PAHs was also obtained. Comparison of Nano-MOUDI mass concentration with that of collocated SMPS was also performed. Upon completion of each site's sampling, the substrates were split into two pieces. Three-fourths were sent to Dr. Tony Miguel (UCLA) for organics analyses, and one-fourth was sent to Rancho Los Amigos for ion chromatography.

Results
Higher mass concentration levels (Size range 2500-0 nm) (Table 2) at all sites are observed in the autumn than in the winter or summer. Riverside, a receptor site, has higher fall and summer mass concentration, as compared to the winter, resulting from increased advection from the Los Angeles basin and photochemical formation of secondary particles. The summer and fall concentrations at USC, a source site, are also higher than the winter. The higher concentration during summer and fall at USC can be explained by the additional contribution of photochemistry to the near-constant traffic background concentrations. Average wintertime mass concentration is higher at the source sites than the receptor sites. At Long Beach the

concentration is higher in spring than winter, which may be an effect of additional particle formation by means of nucleation, a process that may be favored by the foggy conditions of that site at that time of the year. Higher concentrations of nitrate and sulfate were found in the larger particles and no observable levels of these compounds were detected in the 0-56 nm size range for any site at any season. Mass concentration ratios between SMPS and the nano-MOUDI showed lower values for smaller particles and higher values for larger particles, possibly due to the lower density of ultrafine agglomerates. Because of their low density, a substantial fraction of these particles would be classified by an inertial separator (such as the nano-MOUDI) in smaller size bins than if measured by the SMPS, which would classify these irregularly shaped particles in larger size ranges due to their higher surface areas and aerodynamic drag. Table 3 shows size fractionated SMPS vs nano-MOUDI mass concentration ratios for fall, winter and summer at three sites.

The following figures show the size fractionated normalized ultrafine mass concentrations as a function of particle size. Figures 1-4 represent data obtained from USC, Long Beach, Riverside, and Upland, respectively during summer.

Of all the four sites, USC has the highest ultrafine (180-0 nm) mass concentration in summer (2.04 µg/m3). Its vicinity from the freeway may explain the high ultrafine levels at USC. Vehicular pollution mainly emits particles in that size range. Ultrafine mass concentration is also found to be high at Riverside (1.53 $\mu g/m^3$) and Upland (1.41 $\mu g/m^3$) as compared to Long Beach (0.86 $\mu g/m^3$) during summer. The higher values at Riverside and Upland, which are receptor sites, are due to summertime advection from the Los Angeles Basin and photochemical secondary particle formations**.**

Table 2. Seasonal Mass Concentration in (µg/m^3)

Seasons Sites	Fall	Winter	Spring	Summer
USC	29.72	19.04		22.82
Riverside	25.10	8.4		18.94
Long Beach	21.43	13.06	18.96	8.30
Upland	20.97	17.24		9.68

Table 3. Size fractionated SMPS vs NanoMOUDI mass concentration ratios

Aerodynamic Diameter (nm)	Long Beach (Fall)	Long Beach (Summer)	Riverside (Fall)	USC (Fall)	USC (Winter)
1000-320	3.18	2.47	2.33	1.94	1.72
320-180	2.00	2.42	2.06	2.30	1.94
180-100	0.94	1.77	1.89	0.63	2.30
100-56	0.62	0.76	1.11	0.36	1.18
56-32	0.08	0.22	0.35	0.28	0.45
32-10	0.001	0.03	0.12	0.15	0.23

Next Quarter

The chemical analyses for the spring and summer sampling period will be completed and presented in the next report.

Figure 1: USC Ultrafne PM Summer2003
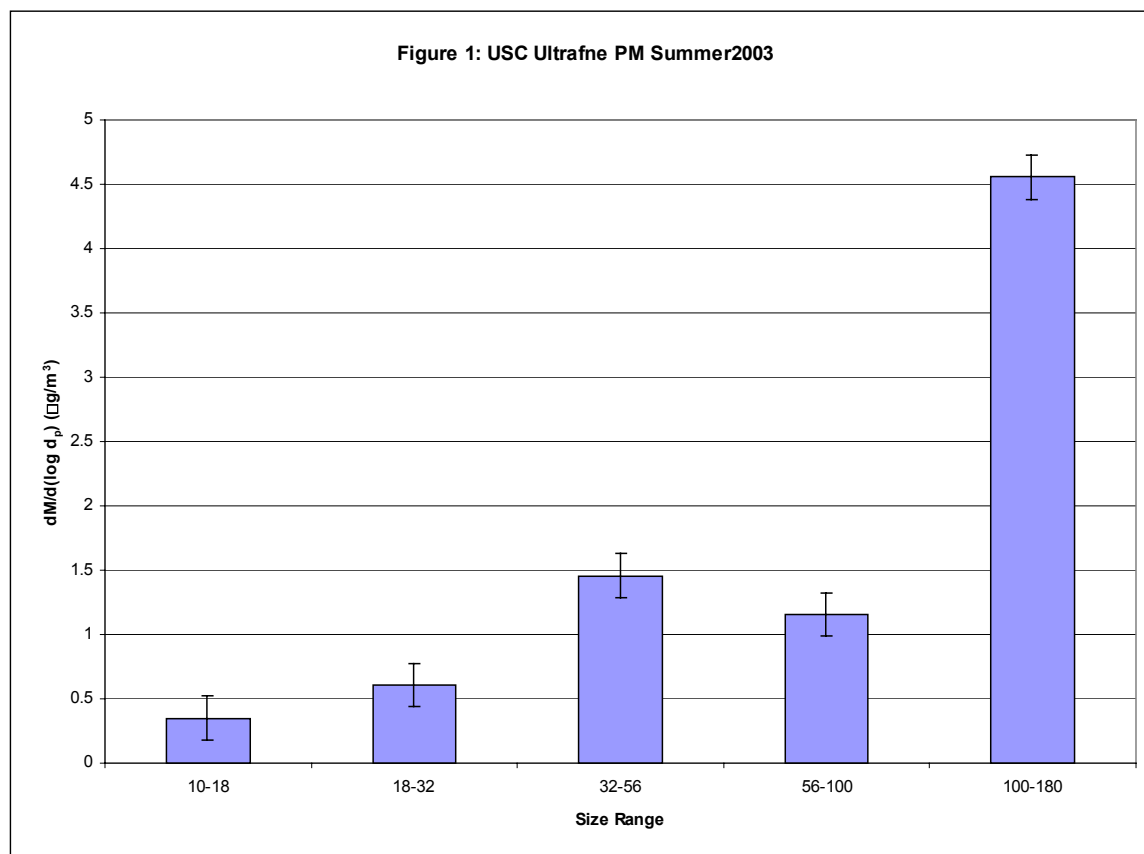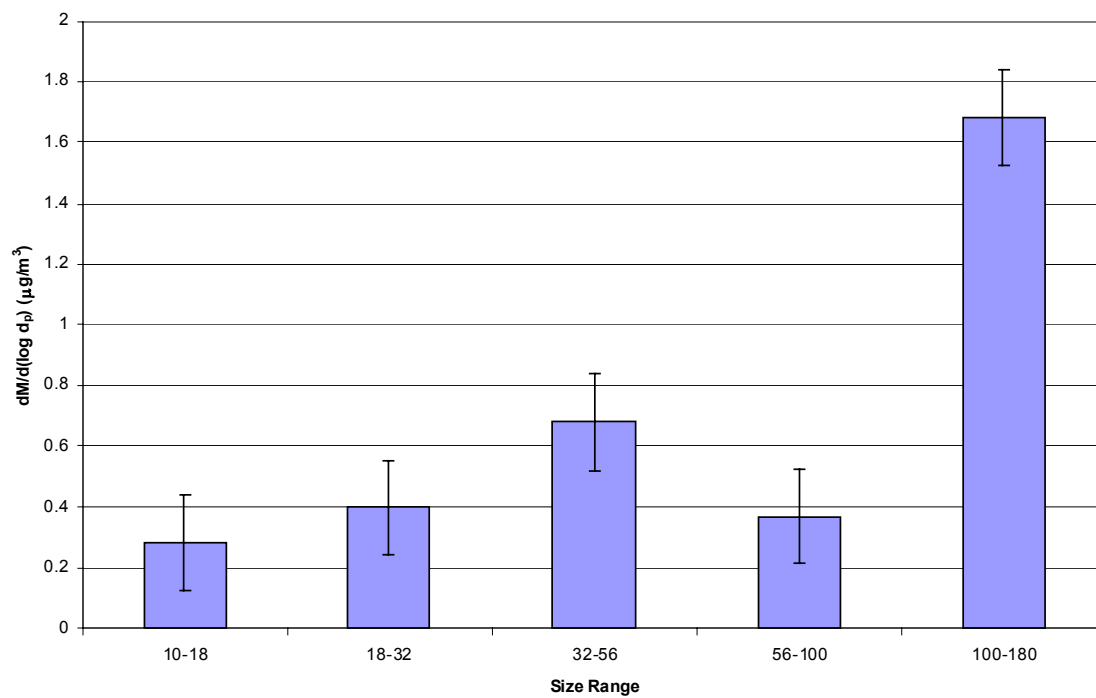
Figure 2: Long Beach Ultrafine PM Summer 2003
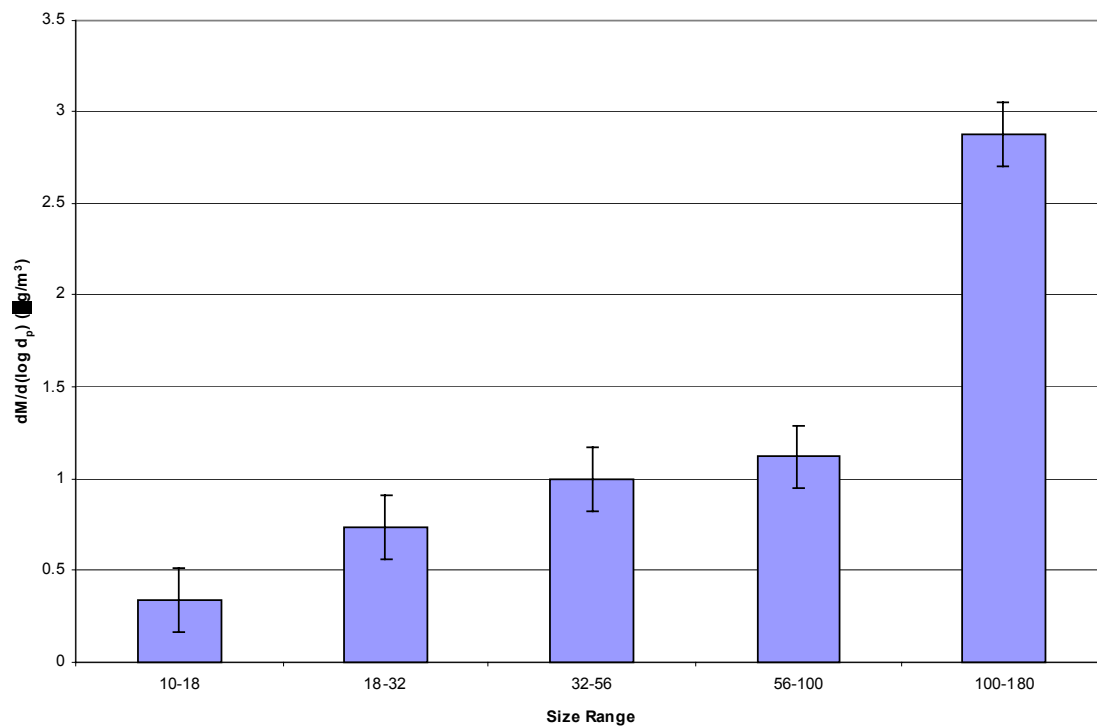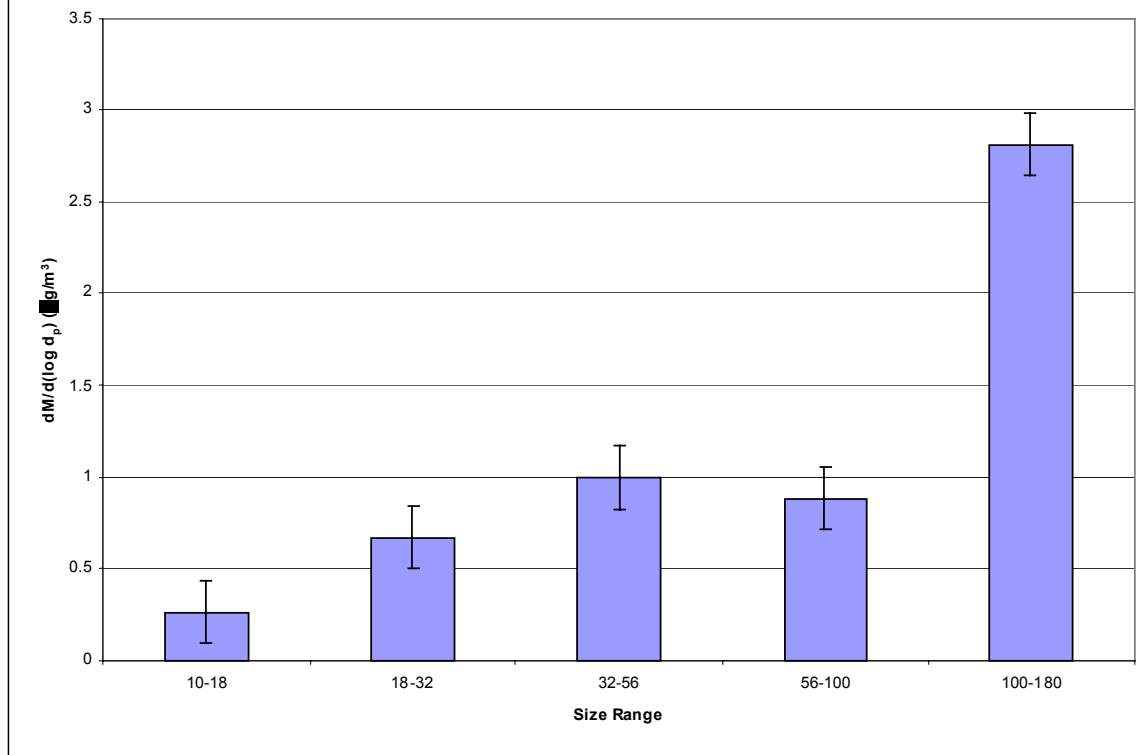

Figure 3: Riverside Ultrafine PM Summer 2003

Figure 4: Upland Ultrafine PM Summer 2003

8. Automated, Size- and Time-Resolved Measurements of Particulate Carbon and Nitrate

Data collection has ended at the USC site for both the Carbon and Nitrate ICVS's from Aerosol Dynamics Inc. Data have been validated and submitted for the period through May 6, 2003. The carbon system continues to run, though data after May 6, 2003 will not be validated at this time. The last valid nitrate data were on April 3, 2003 before a pump failure occurred. Both instruments will be removed and returned to Aerosol Dynamics in June.

During this period, we also conducted a study in which we report a comparison of the results from the Differential Tapered Element Oscillating Microbalance (TEOM) and a semi continuous nitrate monitor in an attempt to obtain insights into the dynamics of volatilization from the heated TEOM filter. Measurements were conducted in Claremont California, a city downwind of Los Angeles and a region of high nitrate concentrations. Field results are compared with that obtained in the laboratory for sampling of pure ammonium nitrate aerosol, and with the vaporization losses predicted by theory. The primary hypothesis that we are testing is that the rate of ammonium nitric acid and ammonia gas volatilization from particle-bound ammonium nitrate that is loaded on the TEOM's fiber filter occurs over time scales that are longer than the five-minute cycle time for the system. This is important to the use of the Differential TEOM, which utilizes the vaporization measured during alternate five-minute periods as a reference baseline value for its particle mass measurements.

Our experiments showed that under ambient conditions, the mass lost from the Differential TEOM tracks well the ambient particulate nitrate concentration. The saturation ratio for nitrate vapor immediately downstream of the filter, calculated at the filter temperature assuming all volatilized mass is ammonium nitrate, ranged from 0.05 to 0.2. By comparison, for laboratory collection of ammonium nitrate aerosol the vaporization reached a maximum value corresponding to a saturation of nitrate vapor downstream of the heated filter. This difference is due to the relatively higher particle concentrations used for the laboratory experiments. For the ambient measurements the particulate nitrate concentrations were consistently lower than the equilibrium vapor concentration at the TEOM filter temperature. In both cases the nitrate vaporization is driven by the temperature of the TEOM filter and independent of the pressure

drop across the filter. These results are described in a manuscript currently in preparation for submission to *Atmospheric Environment* and they will be presented in greater detail in our next Supersite progress report.

9. Quality Control of Semi-Continuous, Mobility Size-Fractionated Particle Number Concentration Data and 2nd Quarter Data Management

This section summarizes the results and conclusions of a methodology study for quality control of SMPS data, which has been accepted for publication (on September 4, 2003) in a coming Supersite Special Issue of <u>*Atmospheric Environment*</u>.

Summary

As part of the quality control efforts at LA Supersite, we developed a two-stage graphic and statistical procedure to label and identify potentially discordant observations. The first stage considered the entire size-fractionated data by date-time as a whole to plot total concentration (TC) vs. coefficient of variation (CV), both in log scale. TC represents the magnitude of overall concentration for a size distribution; while CV represents the relative variability. This plot was used to partition all size distributions into four to five distinct regions. In each region, a generalized extreme studentized deviate (ESD) and a modified Z-score procedure were applied to identify potential discordant outliers. We have found that the majority of particle size distributions are concentrated within a 'normal' region, with TC ranging from 10^2 to 10^5 # cm^{-3} and CV varying between 20 to 200%. Size distributions that are contaminated with discordant outliers are displayed distinctly from the 'normal' region and form four to five clusters in the LogTC-LogCV plot. The pattern of clusters in the plot is consistent among the four sampling sites in this study, suggesting the robustness of this technique. The generalized ESD and modified Z score effectively identify discordant outliers and reveal that the pattern of clustering outliers are consistent within each distinct region. It has, thus, been concluded that the new approach is a useful quality control tool to identify potential discordant outliers in SMPS data.

Results

Figures 1A & 1B demonstrate that similar clustering patterns exist in log TC - log VC plots. In essence, a 'normal' cloud of size distributions is clustered between TC 10^2 to 10^5 # cm^{-3} (logTC = 2 to 5) and CV between 20 to 200 % (logCV = 1.3 to 2.3). The remaining size distributions are apparently contaminated with discordant outliers in four to five distinct regions (A1, A2, A3, A4, and DL), each representing a unique contamination mechanism. The size distributions in the 'A1' region are typical with large TC, but low CV. In contrast, those in the 'A2' region result in high CV (about 2.5 above), but low TC (similar to those in the 'normal' region). In the 'A3' region, the size distributions were both high in TC and CV. There are few distributions in extreme high log TC (>9) and large log CV, as shown in the 'A4' region, exclusive to the Claremont site. A few distributions were labeled with 'DL' because these size distributions are rich in concentrations near or below detection limits.

Figure 2 shows how individual discordant outliers affect typical size distributions of the SMPS, representing the 'Normal,' 'A1,' 'A2,' and 'A3' regions of Figure 1. The size distribution in the 'Normal' region (Figure 2A) shows a typical size distribution profile, without any unexpected discordant outliers. Relatively moderate and extremely high values of particle concentrations have been detected occasionally, leading the CV and TC far away from the 'Normal' cloud and placing them into 'A2' and 'A3' regions (Figure 2B). After removing spike-like observations from the 'A2' and 'A3' regions, the corresponding size distributions might be considered somewhat 'normal'.

Conclusions

1)   Discordant outliers did occur in the particle size distributions generated by the SMPS system.

2)   These outliers contaminated 'normal' particle size distributions in a manner that result in a clustering pattern found unique to the LogTC-LogCV plot. The pattern consists of more than four or five regions in which clusters of particle size distributions are typical.

3)   Overall, for 4 separate monitoring sites, the rate of discordant outliers occurring in SMPS particle size distributions was approximately 0.021%.

Recommendations

1)   The LogTC-LogCV plotting procedure is recommended for automatically screening original SMPS output data to identify outlier-containing size distributions.

2)   The Generalized ESD procedure is recommended for identifying individual outliers in outlier containing size distributions of SMPS data.
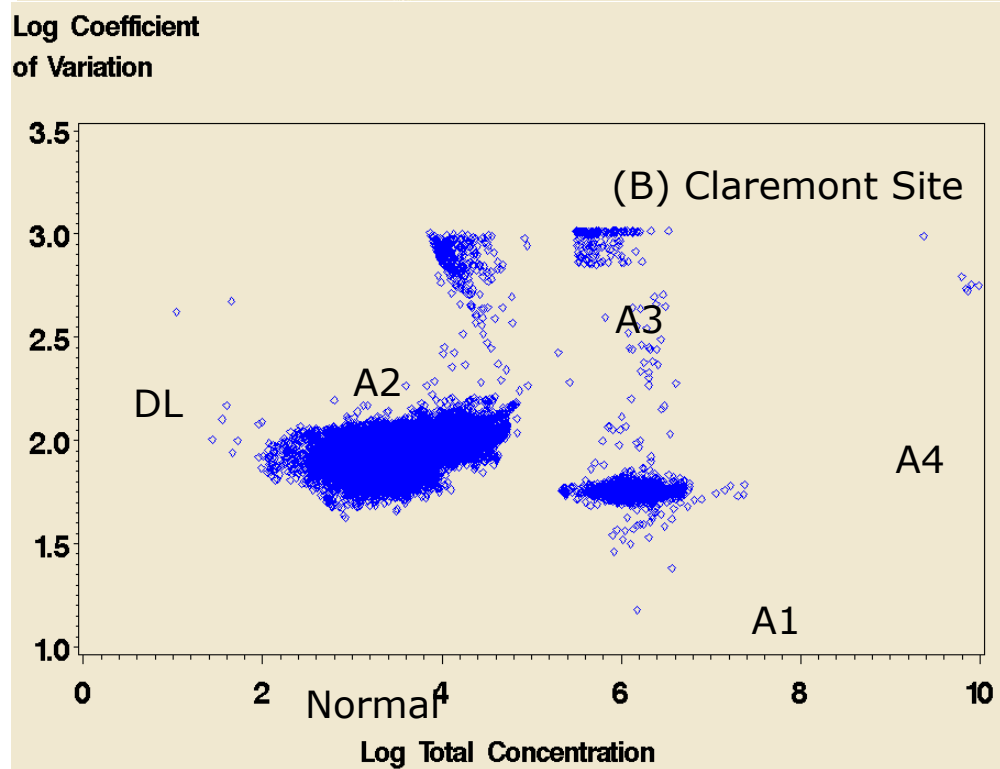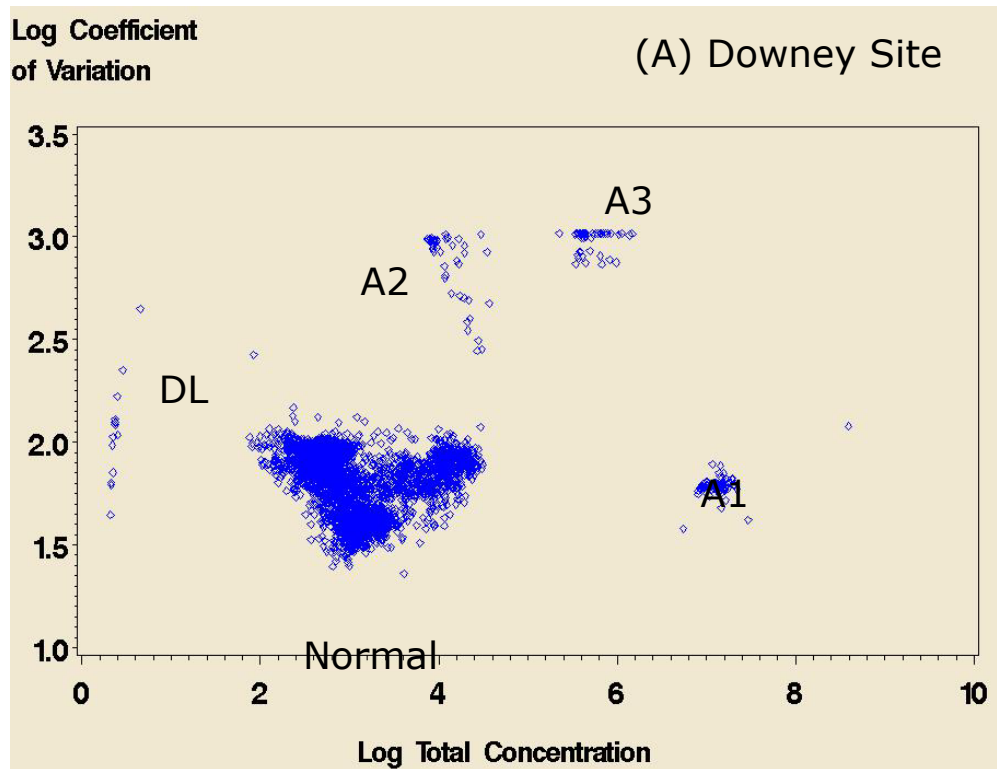
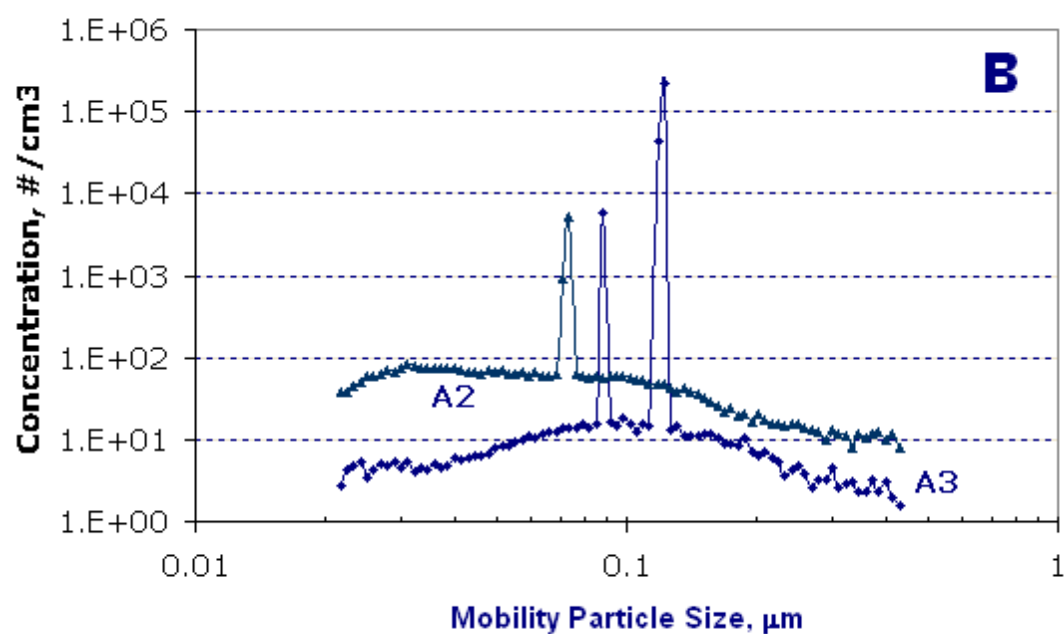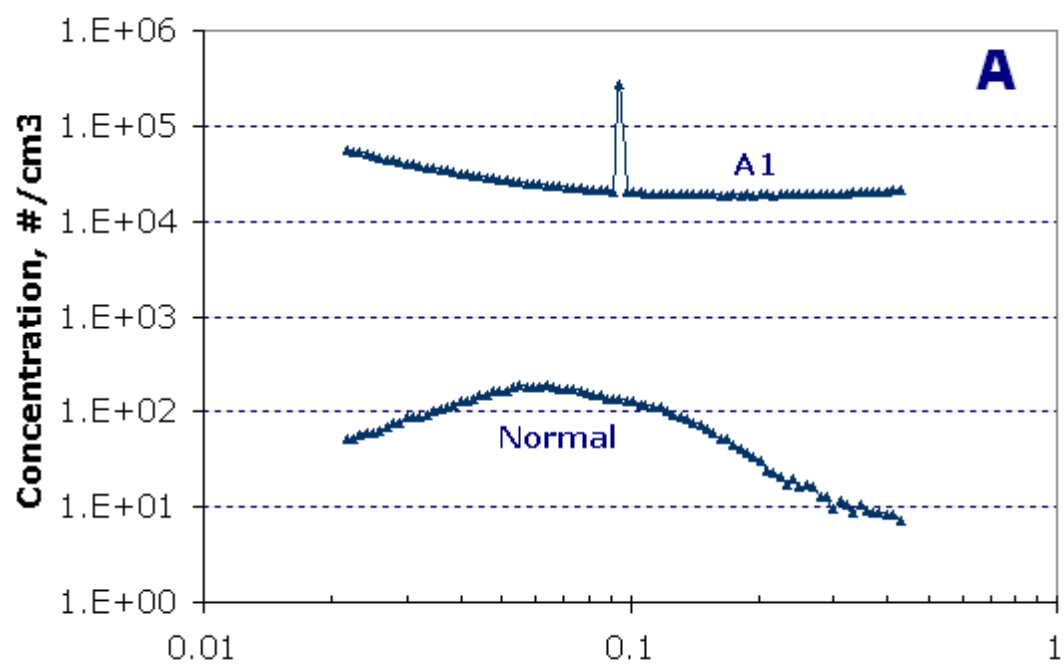Figure 1 SMPS data in Log TC vs. Log CV plots.

Figure 2 Patterns of discordant outliers in different "regions"

B. Uncertainty in MOUDI Metal/Element and SMPS Data

We started to deal with the uncertainty of Supersite data submitted to NARSTO. In this report, methods of MOUDI metals/elements and SMPS data were used.

MOUDI Metals/Elements

Most of our Supersite MOUDI samples were analyzed by the Chester lab. They sent back the report of analytical values and uncertainty for all elements and metals. The uncertainty values are referred as "sigma" values. The reported analytical values were compared with "3*sigma" to ensure sufficient precision to considered as valid. The reported uncertainty values (in ug/filter) were converted into concentration values (in ug/m3), which will be sent along with MOUDI metals and elements to NARSTO.

SMPS (Model 3934)

A formula for calculating uncertainty of SMPS was reported in the page 5-45 of Model 3934 SMPS (Scanning Mobility Particle Sizer) Instruction Manual (P/N 1930081, revision F, October 2002) at http://www.tsi.com/particle/downloads/manuals/1930081f-3934.pdf, as follow:

$$\text{Uncertainty} = \frac{\sqrt{N}}{N}$$

Where N = (particle) counts in a particle size channel.

At LA Supersite, we reported SMPS data on the basis of particle concentration (# of particle per cubic centimeter, #/cm^3). In order to calculate the uncertainty of SMPS concentration values, we modify the uncertainty formula as follow:

$$\textbf{Uncertainty (\%)} = \left[\frac{\sqrt{N}}{N}\right] * 100\% = \left[\frac{\frac{\sqrt{N/V}}{\sqrt{V}}}{N/V}\right] * 100\%$$

$$= \left[\frac{\sqrt{Conc}}{Conc}\right] * \left[\frac{100\%}{\sqrt{V}}\right]$$

where *Conc.* represents particle concentration (#/cm^3) of a particular channel sampling at *F* flow rate (lpm) for *T* minutes. *V* represents the volume of air (cm^3), which is equal to *V* (cm^3) = *F* (lpm) * *T* (min) * 1000 (cm^3/liter). In typical settings of LA Supersite SMPS Model 3934, *F* = 0.3 lpm; *T* = 15 min, yielding *V* = 4,500 (cm^3). Thus,

$$\text{Uncertainty } \textbf{(\%)} = \left[\frac{\sqrt{Conc}}{Conc}\right] * \left[\frac{100}{\sqrt{4,500}}\right]\% = 1.491 * \left[\frac{\sqrt{Conc}}{Conc}\right]\%$$